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(54) Title: BIODEGRADABLE STARCH DERIVATIVE COMPOSITIONS		
(57) Abstract <p>The present invention provides a composition, including a melt, comprising at least one starch derivative and at least one compound having a molecular weight of less than about 3,000 and having at least one ester group and optionally further comprising at least one hydroxyl group. The invention further provides the use of a compound having a molecular weight of less than about 3,000 and having at least one ester group and optionally further comprising at least one hydroxyl group as a processing aid in the manufacture of said composition, as well as methods of making said composition.</p>		

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5 Biodegradable starch derivative compositions.

Field of the Invention

10 The present invention relates to biodegradable polymer compositions capable of being formed by heat and pressure into articles having good dimensional stability and physical properties. These compositions comprise one or more derivatives of starch, and a selected plasticizer.

15 Background of the Invention

It is known that natural starch which is found in vegetable products and which contains various amounts of different plasticizers can be treated at elevated temperatures to form a melt. It is also known that said starch under these conditions can be mixed with synthetic thermoplastic polymers to form a uniform melt which can be formed into various shaped articles. Such articles formed by different techniques such as injection molding, extrusion, co-extrusion, blow molding or foaming have found various applications.

20 An important property of said articles is their capacity to be biodegraded. In humid air, however, these articles tend to absorb and/or adsorb water thereby increasing their moisture content which may lead to a diminution in their hitherto good physical properties. Alternatively, they may dry out under conditions of low humidity and thus become brittle.

35 It is an object of the present invention at least to reduce the disadvantages mentioned above and to provide a biodegradable material with improved water resistance and improved physical properties at high and low humidity levels.

40

Summary of the Invention

According to the present invention, there is provided a composition comprising at least one starch derivative, and
5 at least one compound having a molecular weight of less than about 3,000 and having at least one ester group. The compound may optionally further comprise at least one hydroxyl group.

10 The starch derivative may be selected from the group consisting of starch esters and starch ethers, and the degree of substitution of said starch derivative may be up to about 1.5, and preferably is greater than about 0.8.

15 The starch ester may be a mixed ester, i.e. having different kinds of ester groups attached to the same molecule, as are obtained for example by reaction of starch with a mixed acid anhydride or a mixture of different acid
20 anhydrides. Such a mixed acid anhydride may be for example an acid anhydride made from acetic acid and propionic acid; a mixture of different acid anhydrides may be for example a mixture of acetic acid anhydride and propionic acid anhydride.

25 The starch derivative preferably has an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%.

The compound may be, for example, a glycolmonoester; a
30 mono- or diester of glycerol; a mono-, di- or triester of erythritol; a polyester of pentaerythritol; a mono-, di- or triester of citric acid.

The compound may have a molecular weight of between about
35 100 and about 1,000 and may be present in the composition in an amount of from about 3% to about 60% by weight based on the weight of the composition.

The starch derivative is surprisingly well plasticised by

the compound and the composition yields products with enhanced moisture resistance and which exhibit good physical properties under conditions of high or low relative humidity.

5

The composition may further comprise one or more compounds selected from the group of water-soluble and/or water-swallowable polymers and one or more hydrophobic thermoplastic polymer(s) which is/are substantially water-insoluble.

10

The composition may still further comprise at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, stabilisers, colouring agents, flame retardants, boron-containing compounds and alkali and alkaline earth metal salts.

15

The present invention further relates to compositions in the form of a melt, comprising a derivative of starch, and a compound having a molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group.

20

The present invention still further relates to shaped articles, including a granulate or pellet, made from said composition or melt.

25

The melted compositions may be further processed into shaped articles by a process selected from the group consisting of: injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, co-extrusion, foaming, and combinations thereof.

30

The present invention still further relates to the use of a compound having a molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group as a processing aid in the manufacture of a composition comprising at least one

35

derivative of a starch, and optionally one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

5 The present invention still further relates to a method of preparation of said composition comprising:

(i) drying or conditioning a composition comprising a derivative of a starch to a moisture content of less than about 5%, (ii) admixing to said composition before, during
10 or after drying, at least one compound having a molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group and (iii) melting and plasticising the mixture until a uniform melt is obtained.

15

The present invention still further relates to a method of preparation of said composition, comprising:

(i) melting and plasticising a composition comprising a derivative of starch, and at least one compound having a
20 molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group, until a uniform melt is obtained and (ii) drying the mixture during or after melt formation and/or plastification to a moisture content of less than 5%, by
25 weight of the total composition.

The invention will be further apparent from the following description, in conjunction with the following examples and the appended claims.

30

Detailed Description of the Invention

The present invention refers to a composition comprising, at least one starch derivative, and a compound having a
35 molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group.

The starch derivative preferably is selected from the group

consisting of starch esters and starch ethers, wherein the degree of substitution of said starch derivative is up to about 1.5.

5 The starch ester may be a mixed ester comprising at least two different types of alkylcarbonyl groups (i.e. of different lengths) in the same molecule and as such may be of the kind as obtained by reaction of starch with a mixed anhydride or with a mixture of different acid anhydrides.

10

It is most preferred that such mixed starch esters comprise at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate residues bound to a common starch

15

Particularly preferred starch diesters comprise both acetate and propionate groups or both acetate and butyrate groups or both propionate and butyrate groups or both

20

pentanoate and butyrate groups bound to a common starch molecule.

In the case of starch diesters, the ratio of the types of ester groups comprised by the starch ester may vary

25

greatly, but preferably is in the range of about 1:1 to about 1:20.

Said derivative is made according to known methods from at least one member selected from the group consisting of

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starches of vegetable origin, which starches may be derived from potatoes, rice, tapioca, corn, pea, rye, oats, wheat, maize and barley.

It is preferred that the degree of substitution of said

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derivative is at least 0.8, more preferred that the degree of substitution is from about 0.8 to about 1.45, and most preferred that the said degree is from about 1.0 to about 1.45.

The derivative may be a starch ester selected from the group consisting of acetates, propionates, butyrates and the starch esters of C5 to C12 fatty acids. It is preferred that the derivative is a starch acetate. It is
5 more preferred that the starch acetate has a degree of substitution of from about 0.8 to about 1.45, and most preferred that the acetate has a degree of substitution of from about 1.0 to about 1.45.

10 The derivative may, however, be a starch propionate, in which the degree of substitution is from about 0.8 to about 1.45, and more preferably is from about 1.0 to about 1.45.

The derivative may be an ether and may be selected from the
15 group consisting of alkyl ethers, hydroxyalkyl ethers, hydroxyalkyl-alkylethers and mixtures thereof.

It is preferred that said ether derivative is selected from the group consisting of methylether, ethylether,
20 propylether, butylether, hydroxymethylether, hydroxyethylether, hydroxypropylether, hydroxyethylmethylether and hydroxypropylmethylether and derivatives thereof.

25 In one embodiment of the composition, the starch derivative may have an amylose content of up to about 95% by weight with respect to that of the starch.

In a further embodiment, the amylose content is up to about
30 85% by weight with respect to that of the starch.

In a still further embodiment, the derivative has an amylose content of up to about 75% by weight with respect
to that of the starch.

35

In a still further embodiment, the derivative has an amylose content of up to about 65% by weight with respect to that of the starch.

In a still further embodiment, the derivative has an amylose content of up to about 45% by weight with respect to that of the starch, and in a still further embodiment, the amylose content is between about 30 and about 35% by weight with respect to that of the starch.

The minimum amylose content of the starch preferably is between about 10 and about 15% by weight with respect to that of the starch.

10

The starch derivative has an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%. More preferably, the starch derivative has an equilibrium moisture content of less than about 5%, and most preferably, the derivative has an equilibrium moisture content of less than about 2%.

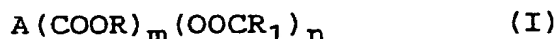
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It is preferred that the compound has a molecular weight of less than 2,000, and more preferred that the molecular weight is between about 100 and about 1,000. It is most preferred that the compound has a molecular weight of between about 200 and about 500.

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The preferred embodiments of the compound may be summarized by the formula:

25



wherein: A is a saturated or unsaturated aliphatic or alicyclic residue; n is an integer from zero to 8; m is an integer from zero to 6; whereby the sum of m + n is an integer from 1 to 6, and R and R₁ are, independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having from 1 to 20 carbon atoms.

30

In one embodiment of compound (I), A is a saturated aliphatic residue having 2 to 8 carbon atoms; m is an integer from zero to 4; n is 0, 1, 2 or 3; the sum of m + n is 2 to 4; and R, and R₁ are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.

35

In a more preferred embodiment of compound (I), A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; m is an integer from zero to 4; n is 0, 1 or 2; the sum of m + n is 2 to 4; and R and R₁ are independent of each other
 5 are alkyl residues having 1, 2, 3 or 4 carbon atoms.

The compound of formula (I) may be an ester derivative of at least one of the following members:

- i) OH-CH₂-(C(COOH)H)_q-CH₂OH
- 10 ii) HOOC-CH₂-(C(COOH)H)_r-CH₂-COOH
- iii) HOOC-CH₂-(C(COOH)OOCR₂)-CH₂-COOH
- iv) HOOC-CH₂-CH((COOH)(COOH)H)
- v) C(CH₂COOH)₄
- vi) (HOCH₂)₃C-O-C(CH₂OH)₃
- 15 vii) HO-CH₂-(CHOH)_q-CH₂OH

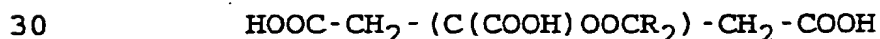
wherein: q and r are independently of each other 1, 2, 3 or 4 and R₂ is methyl or propyl.

The compound of formula (I) may be a methyl, ethyl, propyl, or butyl carboxylate ester of a member selected from the group consisting of:

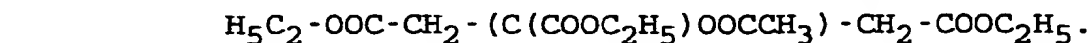
- ii) HOOC-CH₂-(C(COOH)H)_r-CH₂-COOH
- iii) HOOC-CH₂-(C(COOH)(OOCR₂))-CH₂-COOH
- iv) HOOC-CH₂-CH((COOH)(COOH)H)

25 where R₂ is methyl or propyl.

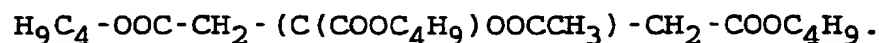
In one embodiment of the compound (I) it is preferred that the carboxylate ester is a tri-ethyl or tri-butyl carboxylate ester of:



where R₂ is methyl or propyl, and it is most preferred that compound (I) is selected from the group consisting of



35 and



Such most preferred compounds of formula (I) are known, and are, for example, sold under the Tradename of Citroflex A-2

plasticisers by Pfizer AG of Fluelastrasse 7, Postfach 2, 8048 Zuerich, Switzerland.

Another embodiment of compound (I) takes the form of a mono, di or tri ester of:

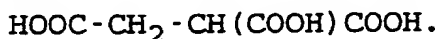


viz the mono-, di-, or tri- acetate of glycerol.

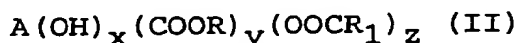
It is most particularly preferred that compound (I) is the tri-acetate of glycerol, viz:



Compound (I) may also be a diacetate-monopropionate or dipropionate-monoacetate of glycerol or the diacetate or dipropionate of $\text{OH}-\text{CH}_2-\text{C}(\text{COOH})\text{H}-\text{CH}_2\text{OH}$, or it may be selected from the trimethyl ester and tripropyl ester of:



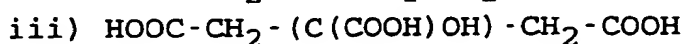
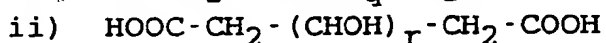
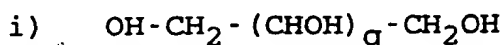
In a further preferred embodiment of the composition of the present invention, the compound has the formula:

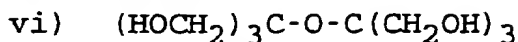
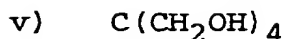
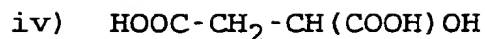


wherein A is a saturated aliphatic residue having 2 to 8 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y+ z is 2 to 4; and R and R_1 are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.

In a more preferred embodiment of compound (II), A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y+ z is 2 to 4; and R and R_1 are independent of each other are alkyl residues having 1, 2, 3 or 4 carbon atoms.

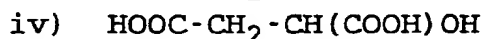
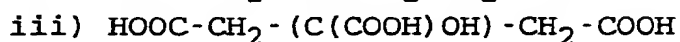
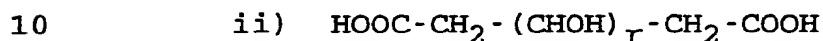
The compound of formula (II) may be an ester derivative of at least one of the following members:





wherein: q and r are independently of each other 1, 2, 3 or 4.

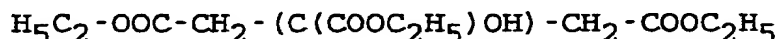
It is preferred that compound (II) is a methyl, ethyl, propyl or butyl carboxylate ester of a member selected from the group consisting of:



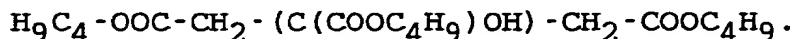
It is more preferred that the carboxylate ester is an ethyl or butyl ester, and it is most preferred that the compound is a tri-ethyl or tri-butyl carboxylate ester of:



Accordingly, the most preferred compounds of formula (II) have the formulae:



or

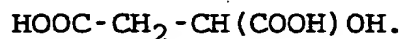


Such most preferred compounds are known, and are, for example, sold under the Tradename of Citroflex plasticisers by Pfizer AG of Fluelastrasse 7, Postfach 2, 8048 Zuerich, Switzerland.

Other forms of compound (II) for use according to the present invention include the diacetate and dipropionate of:



and the monoacetate-dimethyl ester and mono-acetate-dipropyl ester or mono-propionate-dipropyl ester of:



The compound, whether of formula (I) or (II) is present in the composition in an amount of from about 3% to about 60%

by weight based on the weight of the composition. It is more preferred that the concentration of compound in the composition is from about 5% to about 30%, and most preferred that the concentration of the compound in the composition is from about 8% to about 18% by weight based on the weight of the composition.

The composition according to this invention may further comprise in an amount of up to 40%, and preferably up to 30 % by weight of the total composition one or more compounds selected from the group of water-soluble and/or water-swella-ble polymers. This group includes a large number of known polymers such as water-soluble celluloses such as: alkylcelluloses, hydroxyalkylcelluloses and hydroxyalkylcelluloses, such as: methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, cellulose esters and hydroxyalkylcellulose esters such as: cellulose acetylphthalate (CAP), Hydroxypropylmethylcellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcellulose esters such as: carboxymethylcellulose and their alkali-metal salts; water-soluble or water-swella-ble synthetic polymers such as: poly(acrylic acids) and their salts and essentially water soluble poly(acrylic acid) esters, poly(methacrylic acids) and their salts and essentially water-soluble poly(methacrylic acid) esters, essentially water soluble poly(vinyl acetates), poly(vinyl alcohols), poly(vinyl acetate phthalates) (PVAP), poly(vinyl pyrrolidone), poly(crotonic acids); cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and mixtures of such polymers. Preferred from the group of poly(vinyl-alcohols) are alkenol homopolymers and alkenol copolymers.

The alkenol homopolymer is preferably a polyvinyl alcohol

which may be hydrolysed to an extent of from about 45 mol% and about 100 mol% and preferably from about 85 mol% to about 99.8 mol% and most preferably from about 96 mol% to about 99.8 mol%. For increased moisture resistance a degree of hydrolysis of about 97 mol% to about 99.8 mol% is preferred. The number average molecular weight ranges preferably from about 15,000 to about 250,000, and more preferably from about 50,000 to about 150,000. Most preferred is a molecular weight ranging from about 80,000 to about 120,000. Likewise, for increased moisture resistance a higher molecular weight, preferably of between about 100,000 and about 120,000 is preferred.

One embodiment of the composition contains pre-treated polyvinyl alcohol in the form of a melt, obtained previously by adding sufficient energy to polyvinyl alcohol to melt it and substantially eliminate crystallinity in the melt. It is particularly preferred that the such crystallinity is substantially completely eliminated.

Alkenol copolymers as mentioned above are preferably synthetic copolymers containing vinyl alcohol units as well as aliphatic units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate with monomers preferably ethylene, propylene, isobutylene and/or styrene with subsequent complete or partial hydrolysis of the vinyl ester group. These copolymers have a sufficient hydroxyl group content that they remain at least water-swellaable within the definition as given herein.

The present inventive composition may further comprise in an amount up to 60 %, preferably in an amount up to 35% and most preferably in an amount up to 25% by weight of the total composition, one or more hydrophobic thermoplastic polymer(s) which is/are substantially water-insoluble. Such a polymer is one that dissolves water at a rate of less than 25 grams per 100 grams of the dry polymer, and more preferably at a rate of less than 15 grams per 100 grams of dry polymer when immersed in water at room

temperature. Examples of hydrophobic thermoplastic polymers are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes, vinylpolymers such as poly(vinyl chloride) (PVC), poly(vinyl acetates), polystyrenes; polyacrylonitriles (PAN); polyvinylcarbazoles (PVK); substantially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates such as polyamides (PA), thermoplastic polyesters, polycarbonates, polyurethanes, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; but also poly(hydroxybutyrate) (PHB) and high molar-mass, substantially water-insoluble poly(alkylene oxides) such as polymers of ethylene oxide and propylene oxide as well as their copolymers are included.

Further included are hydrophobic thermoplastic copolymers of the different kinds known such as ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVOH); ethylene/acrylic acid-copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS - copolymers; styrene/acrylonitrile-copolymers (SAN); and mixtures thereof.

Preferred from these are those with a set processing temperature preferably within the range of 95°C to 210°C, preferably within the range of 95°C to 190°C.

Also preferred are polymers containing polar groups such as hydroxyl, ether-, acid, ester or urethane groups. Such polymers include, for example, copolymers of ethylene, propylene or isobutylene such as ethylene/vinyl acetate-copolymers (EVA), ethylene/vinyl alcohol-copolymers (EVOH), ethylene/acrylic acid-copolymers (EAA), ethylene/ethyl acrylate-copolymers (EEA), ethylene/methacrylate-copolymers (EMA), polyurethane-copolymers, styrene/acrylonitrile-copolymers (SAN); polyacetals (POM) and their mixtures as mentioned above. The synthetic polymer may contain the usual known processing additives.

The particularly preferred copolymers are ethylene/vinyl alcohol-copolymers having an ethylene content of about 10 mol% to about 50 mol%. Said preferred copolymers may have about 15 mol% to about 48 mol%. ethylene and those polymers
5 having an ethylene content of about 40 mol% to about 48 mol% provide enhanced water resistance.

The composition according to the present invention has a relatively low water content - preferably below 10%, more
10 preferably below 5% and specifically below 2% by weight of the total composition. The moisture content of the composition is therefore reduced either before mixing the compound with the starch derivative or during the melt formation process. For example, it is possible to
15 initiate melt formation of the composition in a vented extruder and to evaporate the moisture from the melt by vacuum just before the melt is extruded.

The present invention also refers to a method of
20 preparation of the compositions according to this invention comprising (i) drying or conditioning a composition comprising a starch derivative to a moisture content of less than 5%, and preferably less than 2% by weight, (ii) admixing to said composition before, during or after
25 drying, a compound having a molecular weight of less than about 3,000 and at least one ester group and optionally further comprising at least one hydroxyl group and (iii) melting and plasticising the mixture until a uniform melt is obtained.

30

Said melt may subsequently be extruded, cooled and cut to form granulates which may optionally be mixed with additives before further processing as explained herein.

35

A further method of preparation of a composition according to this invention comprises (i) melting and plasticising a composition comprising a starch derivative, and a compound having a molecular weight of less than about 3,000 and at least one ester group and optionally further comprising

least one hydroxyl group, until a uniform melt is obtained and (ii) drying the mixture during or after melt formation and/or plastification to a moisture content of less than 5%, and preferably less than 2% by weight of the total composition.

The starch derivative may be mixed with the compound and optionally with further polymers and/or other additives as defined herein in any desired sequence. It is important, however, that the moisture content be reduced to the indicated values latest in the melt stage of the composition. Thus, for example, the derivatised starch may be dried and mixed with all the intended additives, including polymer/s to form the composition, which may then be heated to form a uniform melt.

It is also possible to mix all the components and dry the mixture before melt formation is initiated or, as a further possibility, to dry the composition during melt formation or after the melt has been formed using a vented extruder.

Preferably, however, the derivative is mixed with the compound and other desired additives to form a free flowing powder, which is useful for continuous processing. This powder is fed to the hopper of an extruder, and processed to form a melt which is then solidified. The cooled solidified melt may then be either granulated or further processed into any desired shaped articles.

In order to melt the composition according to the invention, it is suitably heated in a screw and barrel of an extruder for a time sufficient to enable uniform melt formation. The temperature is preferably within the range of 100°C to 220°C, and more preferably within the range of from 160 to 200°C, the precise temperature being dependent up on the type and nature of the composition used. For thermoplastic melt formation of the composition according to the invention, the composition preferably is heated in an extruder, and preferably in a vented extruder for achieving the drying of the composition as explained above.

Pressures created in such a volume correspond to the vapour pressure of the most volatile material present (which may be water) at the used temperature. It will be appreciated that pressures may be applied or generated as is known in the use of a screw and barrel.

The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are known per se, being up to about $150 \times 10^5 \text{ N/m}^2$, more preferably up to about $75 \times 10^5 \text{ N/m}^2$ and most preferably up to about $50 \times 10^5 \text{ N/m}^2$.

Within the screw the granular mixture is heated to a temperature which is generally within the range of about 120 to 220°C , more preferably within the range of about 120 to 190°C and most preferably within the range of about 130 to 190°C .

The minimum pressures under which the melts are formed correspond to the vapour pressures produced at said temperatures. These pressures are recommended even a substantially anhydrous composition is used. Ranges of pressures suitable for extrusion processes are from zero to about $150 \times 10^5 \text{ N/m}^2$, preferably from zero to about $75 \times 10^5 \text{ N/m}^2$ and most preferably from zero to about $50 \times 10^5 \text{ N/m}^2$ whereby for injection molding processes these pressures may exceed $150 \times 10^5 \text{ N/m}^2$.

Optionally the composition comprises at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, stabilisers, flame retardants, boron-containing compounds, alkali and alkaline earth metal salts, and colouring agents.

Examples of extenders of are gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins or rape seed proteins. Such extenders may optionally be added in any desired amount

preferably up to and including 20%, and preferably are within the range of 3 % to 10 % based on the total weight of all the components.

5 Suitable fillers include, for example, oxides of magnesium, aluminum, silicon, and titanium as well as wood derived materials or for example cellulose fibers. The fillers are present in the composition at a concentration of up to about 20% by weight, and preferably between about 3.0 and
10 about 10%, by weight, based on the total weight of the composition.

The lubricants include stearates of aluminum, calcium, magnesium, and tin, as well as the free acid and magnesium
15 silicate, silicones and substances such as lecithin, and mono and diglycerides, which for the purpose of the present invention function in like manner. The particularly preferred lubricants are stearic acid or lecithin, which are present in the composition in amounts
20 of up to 10 parts per 100 parts of starch, preferably in an amount of from 1 to 3 parts per 100 parts of starch, and most preferably is present in the composition in an amount of 1 part per 100 parts of starch.

25 Other plasticisers include low molecular weight poly(alkylene oxides), such as, for example, poly(ethylene glycols), poly(propylene glycols) poly(ethylene-propylene glycols), such as, for example, glycerol; pentaerythritol; propylene glycol; sorbitol; sodium diethylsulfosuccinate;
30 phosphatides of which lecithin is preferred or urea. These plasticisers are preferably present in the composition at a concentration of between about 0.5% and about 15% by weight, and more preferably between about 0.5% and about 5% by weight, based on the weight of all of the components,
35 including the water therein.

Preferably the sum of all the plasticizer in the composition does not exceed about 30% by weight, and most preferably does not exceed about 25% by weight, based on

the total weight of the composition.

5 Stabilisers include antioxidants such as thiobisphenols, alkylidenbisphenols, secondary aromatic amines; stabilisers against photo-decomposition, such as, for example, uv absorbers and quenchers; hydroperoxide decomposers; free radical scavengers, and anti-microbial agents.

10 Colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin.

Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides being present in the composition at a concentration of between about 0.01 and about 10% by weight, and preferably present at a
15 concentration of between about 0.05 and about 3% by weight, based on the total weight of the composition. Most preferably the colouring agents are present in the composition in an amount of about 0.03 to about 0.07% by weight with respect to the total composition.

20 Still further substances which may be added to the composition include animal or vegetable fats, preferably in their hydrogenated forms, especially those which are solid at room temperature. Such fats preferably have a melting
25 point of at least 50°C and include triglycerides of C12-, C14-, C16-and C18- fatty acids.

The total concentration of said fats, mono-, di- glycerides and phosphatides may be up to 5% by weight, based on the
30 total weight of the composition.

The composition may further comprise flame retardants which, for example, comprise phosphorous, sulphur and halogens, or mixtures thereof.

35 Suitable phosphorous-containing flame retardants include diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorous oxide;

aliphatic phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2-ethylhexyl diphenyl phosphate; and tributoxyethyl phosphate. These retardants are available from Akzo
5 Chemicals Inc. of 300 South Riverside Plaza, Chicago, Illinois, USA.

Further suitable phosphorous-containing retardants include: guanidinium phosphate which can be obtained from Chemie
10 Linz GmbH of St Peter strasse 25, A-4021, Linz, Austria; bis(hydroxypropyl) sec.butyl phosphine oxide which can be obtained from the Chemical Products Group of FMC Corporation, 2000 Market Street, Philadelphia, Pennsylvania 19103, USA; and the following compounds obtainable from
15 Albright and Wilson, Americas Inc, of P.O. Box 26229, Richmond, Virginia, 23260, USA: polypropoxylated dibutyl pyrophosphoric acid; a mixture of phosphonic acid, methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl ester, P-oxide and phosphonic acid, methyl-, bis [(5-ethyl-
20 2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl] ester, P,P'-dioxide as sold under the trade name Amgard V19; ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous.

25 Where ammonium polyphosphate and ethylenediamine polyphosphate are used as flame retardants, it is preferred that they are buffered with disodium orthophosphate so that they are thereby less corrosive to the equipment used for
30 processing the composition comprising them.

Suitable sulphur containing-retardants include: guanidinium sulfate obtainable from Chemie Linz GmbH at the address given above; ammonium sulfate; ammonium sulfamate; and
35 tetrakis (hydroxymethyl) phosphonium sulfate; all of which may be obtained from the American Cyanamid Company, of One Cyanamid Plaza, Wayne, New Jersey, 07470, USA.

The particularly preferred flame retardants are ammonium

polyphosphate and/or ethylenediamine polyphosphate, guanidinium phosphate, ammonium sulphate and/or guanidinium sulfate.

5 The above mentioned flame retardants are present in the composition in an amount of from 0.5 to about 15%, preferably from about 1.5 to 8%, and most preferably from 2 to 5%, all percentages being by weight with respect to that of the total composition.

10

Still further compounds which may be added to, or present in the composition include boron-containing compounds, particularly so when the composition is formed into films, sheets or fibers. The presence of such boron compounds in
15 the composition yields articles which have improved transparency, Young's modulus and tear strength. The preferred boron-containing compounds are boric acid, metaboric acid, alkali and alkaline earth metal salts, borax and derivatives thereof. Said boron containing
20 compounds may be present in the composition in an amount of between 0.002 and 0.4%, by weight with respect to that of the composition, and preferably are present at a concentration of between about 0.01 and 0.3%, likewise by weight.

25

Inorganic salts of alkali or alkaline earth metals, particularly LiCl and NaCl may be additionally present in the composition in an amount of between 0.1 and 5% by weight with respect to that of the total composition. The
30 presence of such salts in the composition still further improves the Young's modulus, transparency and tear strength of articles made from the composition.

35

The compositions according to this invention form thermoplastic melts on heating under conditions as described herein. Such melts can be processed just like conventional thermoplastic materials, using, for example, injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, to

produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, rods, laminated films, sacks, bags, foams, pharmaceutical capsules, granules or powders.

5

The composition comprising the starch derivative and the compound may also be used in the form of a masterbatch wherein the compound is present in a high concentration, for example in a concentration of about 40 % to about 80 % by weight relative to the total weight of the masterbatch.

10

The inventions according to this invention may also be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for sustained release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

15

The following examples further explain the invention.

20

Example 1

A composition comprising corn starch acetate with a degree of substitution (DS) of about 1 and citroflex:

25

$\text{H}_5\text{C}_2\text{-OOC-CH}_2\text{-(C(COOC}_2\text{H}_5\text{)OH)-CH}_2\text{-COOC}_2\text{H}_5$ (obtainable from Pfizer at the address given above) in an amount of 45% by weight with respect to that of the starch, together with usual additives is fed into the entry port of a twin screw extruder. The composition is plasticised with mechanical energy being provided by a strong screw configuration (such as is known to those skilled in the art) at a suitable pressure necessary to avoid the formation of vapour at the used temperature.

30

35

The composition is plasticised until a uniform melt is achieved, and thereafter the moisture content of the composition is reduced to about 5% before exit of the composition from the barrel. The melt is formed into

tensile test pieces which exhibit improved Young's modulus, tensile strength and ultimate elongation.

Example 2

Example 1 is repeated except that a high amylose (about 75% by weight) acetate-substituted starch, likewise having a degree of substitution of about 1, is substituted for the corn starch acetate.

The thus formed test pieces are examined likewise for the pieces of Example 1 and the results are similarly good.

Example 3

Example 1 is repeated except that the melted composition comprises 50% by weight with respect to that of the starch of citroflex, and the starches have varying degrees of substitution as shown in Table 1. The compositions are formed into films which exhibit improved water resistance and physical properties, as long as the degree of starch substitution is at least about 0.8.

Table 1

Starch type	DS
Corn starch acetate	0.2
Corn starch acetate	0.4
Corn starch acetate	0.4
Corn starch acetate	1.0
Corn starch acetate	1.45

Example 4

A composition comprising corn starch acetate and citroflex A-2 - $\text{H}_5\text{C}_2\text{-OOC-CH}_2\text{-(C(COOC}_2\text{H}_5\text{)OOCCH}_3\text{)-CH}_2\text{-COOC}_2\text{H}_5$ -

(obtainable from Pfizer at the address given above) in an amount of 45% by weight with respect to that of the starch, together with usual additives is fed into the entry port of a twin screw extruder. The composition is plasticised, with mechanical energy being provided by a strong screw configuration (such as is known to those skilled in the art) at a suitable pressure necessary to avoid the formation of vapour at the used temperature. The starch has a degree of substitution of about 1.

The composition is plasticised until a uniform melt is achieved, and thereafter the moisture content of the composition is reduced to about 5% before exit of the composition from the barrel. The melt is formed into tensile test pieces which are subjected to Young's modulus, tensile strength and ultimate elongation determinations. The results are presented in Table 2.

Example 5

Example 4 is repeated except that a high amylose (about 75% by weight) acetate-substituted starch, likewise having a degree of substitution of about 1, is substituted for the corn starch acetate.

The thus formed test pieces are examined likewise for the pieces of Example 1 and the results are presented in Table 2.

Table 2

	Example 4	Example 5
Degree of Substitution	130	1.1
Young's Modulus (N/mm ²)	130	210
Tensile Strength (N/mm ²)	5	7
Ultimate Elongation (%)	11	38

Example 6

Example 4 is repeated except that the melted composition comprises 50% by weight with respect to that of the starch of citroflex, the starches have varying degrees of substitution as shown in Table 3, and the compositions are formed into films. The films are submerged in water at room temperature for 60 minutes and are then assessed for water absorption capacity. The results are presented in Table 3.

Table 3

	DS	Water uptake (%) without citroflex	Water uptake (%) with citroflex
Corn starch acetate	0.0	216	Sample disintegrates
Corn starch acetate	0.4	222	Sample disintegrates
Corn starch acetate	0.8	21	8
Corn starch acetate	1.0	11	5
Corn starch acetate	1.5	8	2

15 It is clear from Tables 2 and 3 that the addition of the
citroflex plasticizer to the starch derivative yields a
composition which can be formed into articles which have
improved water resistance and physical properties, as long
as the degree of starch substitution is at least about 0.8.

20

It will be appreciated that it is not intended to limit the
invention to the above examples only, many variations
thereto and modifications thereof being possible to one
skilled in the art without departing from its scope, which
25 is defined by the appended claims.

What We Claim is:

1. A composition comprising at least one starch derivative and at least one compound having a molecular weight of less than about 3,000 and having at least one ester group.
2. A composition according to claim 1, in which the compound further comprises at least one hydroxyl group.
3. A composition according to either of claims 1 or 2, in which the starch derivative is selected from the group consisting of starch esters and starch ethers.
4. A composition according to any preceding claim, in which the degree of substitution of said starch derivative is up to about 1.45, and preferably is at least about 0.8.
5. A composition according to any preceding claim, in which the derivative is a starch ester selected from the group consisting of acetates, propionates, butyrates and the starch esters of C5 to C12 fatty acids.
6. A composition according to any preceding claim, in which the derivative is a starch acetate having a degree of substitution of from about 0.8 to about 1.45 or a starch propionate having a degree of substitution of from about 0.8 to about 1.45.
7. A composition according to any preceding claim, in which the starch ester been obtained by reaction of starch with a mixed acid anhydride or with a mixture of different acid anhydrides.
8. A composition according to claim 7, in which the starch ester comprises at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate.

9. A composition according to the preceding claim, in which the starch ester comprises both acetate and propionate groups bound to a common starch molecule, or both acetate and butyrate groups bound to a common starch molecule, or both propionate and butyrate groups bound to a common starch molecule, or both pentanoate and butyrate groups bound to a common starch molecule.

10. A composition according to either of claims 8 or 9, in which the ratio of the members is about 1:1 with respect to the members, or about 1:2 with respect to the members, or about 1:3 with respect to the members, or about 1:20 with respect to the members.

11. A composition according to any one of claims 1 to 3, in which the derivative is selected from the group consisting of alkyl ethers and hydroxyalkyl ethers, hydroxyalkylalkylethers and mixtures thereof.

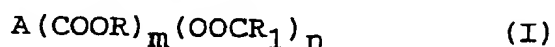
12. A composition according to the preceding claim, in which the ether derivative is selected from the group consisting of methyl ether, ethylether, propylether, butylether, hydroxymethylether, hydroxyethylether, hydroxypropylether, hydroxyethylmethylether and hydroxypropylmethylether and derivatives thereof.

13. A composition according to any preceding claim, in which the derivative has an amylose content of up to about 95% by weight with respect to that of the starch.

14. A composition according to any preceding claim, wherein the starch derivative has an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%.

15. A composition according to any preceding claim, wherein the compound has a molecular weight of less than 2,000, and preferably has a molecular weight of between about 200 and about 500.

16. A composition according to claim 1, wherein the compound has the formula:



wherein: A is a saturated or unsaturated aliphatic or alicyclic residue; n is an integer from zero to 8; m is an integer from zero to 6; whereby the sum of m + n is an integer from 1 to 6, and R, and R₁ are, independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having from 1 to 20 carbon atoms.

10

17. A composition according to claim 16, wherein A is a saturated aliphatic residue having 2 to 8 carbon atoms; m is an integer from zero to 4; n is 0, 1, 2 or 3; the sum of m + n is 2 to 4; and R, and R₁ are independent of each other and are alkyl residues having from 1 - 6 carbon atoms.

15

18. A composition according to claim 16 in which A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; m is an integer from zero to 4; n is 0, 1, or 2; the sum of m + n is 2 to 4; and R, and R₁ are independent of each other are alkyl residues having 1, 2, 3 or 4 carbon atoms.

20

19. A composition according to claim 16, in which the compound is an ester derivative of at least one of the following members:

25

- i) $\text{OH}-\text{CH}_2-(\text{C}(\text{COOH})\text{H})_q-\text{CH}_2\text{OH}$
- ii) $\text{HOOC}-\text{CH}_2-(\text{C}(\text{COOH})\text{H})_r-\text{CH}_2-\text{COOH}$
- iii) $\text{HOOC}-\text{CH}_2-(\text{C}(\text{COOH})\text{OOCR}_2)-\text{CH}_2-\text{COOH}$
- iv) $\text{HOOC}-\text{CH}_2-\text{CH}((\text{COOH})(\text{COOH})\text{H})$
- v) $\text{C}(\text{CH}_2\text{COOH})_4$
- vi) $(\text{HOCH}_2)_3\text{C}-\text{O}-\text{C}(\text{CH}_2\text{OH})_3$
- vii) $\text{HO}-\text{CH}_2-(\text{CHOH})_q-\text{CH}_2\text{OH}$

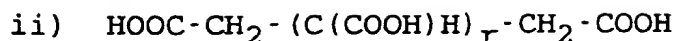
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wherein: q and r are independently of each other 1, 2, 3 or 4 and R₂ is methyl or propyl.

35

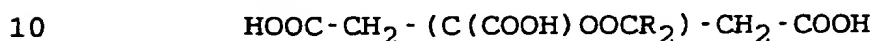
20. A composition according to the preceding claim, in which the compound is a methyl, ethyl, propyl, or butyl carboxylate ester of a member selected from the group

consisting of:



5 where R_2 is methyl or propyl.

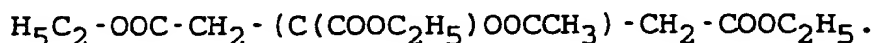
21. A composition according to the preceding claim, in which the compound is a tri-ethyl or tri-butyl carboxylate ester of:



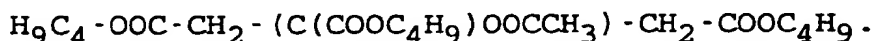
where R_2 is methyl or propyl.

22. A composition according to the preceding claim, in which the compound is selected from the group consisting of

15



and



20 23. A composition according to claim 16, in which the compound is a mono, di or tri ester of:



24. A composition according to claim 23, in which the compound is the tri-acetate of glycerol, viz:

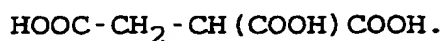
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25. A composition according to claim 16, in which the compound is a diacetate-monopropionate or dipropionate-monoacetate of glycerol or the diacetate or dipropionate of

30

$\text{OH-CH}_2\text{-C(COOH)H-CH}_2\text{OH,}$ or the trimethyl ester or tripropyl ester of:



35 26. A composition according to claim 2, in which the compound has the formula:



wherein: A is a saturated or unsaturated aliphatic or allicyclic residue; x is 1 or 2; y is an integer from zero

to 4; z is an integer from zero to 4, whereby the sum of y + z is 2 to 4 and R and R₁ are, independently of each other, a saturated or unsaturated aliphatic or alicyclic residue having from 1 to 6 carbon atoms.

5

27. A composition according to claim 26, in which A is a saturated aliphatic residue having 2, 3, or 4 carbon atoms; x is one or two; y is an integer from zero to 4; z is an integer from zero to 4; the sum of y + z is 2 to 4; and R and R₁ are independent of each other are alkyl residues having 1, 2, 3 or 4 carbon atoms.

10

15

28. A composition according to claim 26, in which the compound is an ester derivative of at least one of the following members:

20

- i) $\text{OH}-\text{CH}_2-(\text{CHOH})_q-\text{CH}_2\text{OH}$
- ii) $\text{HOOC}-\text{CH}_2-(\text{CHOH})_r-\text{CH}_2-\text{COOH}$
- iii) $\text{HOOC}-\text{CH}_2-(\text{C}(\text{COOH})\text{OH})-\text{CH}_2-\text{COOH}$
- iv) $\text{HOOC}-\text{CH}_2-\text{CH}(\text{COOH})\text{OH}$
- v) $\text{C}(\text{CH}_2\text{OH})_4$
- vi) $(\text{HOCH}_2)_3\text{C}-\text{O}-\text{C}(\text{CH}_2\text{OH})_3$

wherein: q and r are independently of each other 1, 2, 3 or 4.

25

29. A composition according to the preceding claim, wherein the compound is a methyl, ethyl, propyl or butyl carboxylate ester of a member selected from the group consisting of:

30

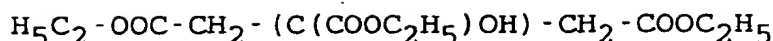
- ii) $\text{HOOC}-\text{CH}_2-(\text{CHOH})_r-\text{CH}_2-\text{COOH}$
- iii) $\text{HOOC}-\text{CH}_2-(\text{C}(\text{COOH})\text{OH})-\text{CH}_2-\text{COOH}$
- iv) $\text{HOOC}-\text{CH}_2-\text{CH}(\text{COOH})\text{OH}$

35

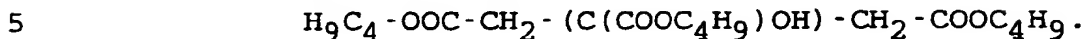
30. A composition according to the preceding claim, wherein the compound is a tri-ethyl or tri-butyl carboxylate ester of:



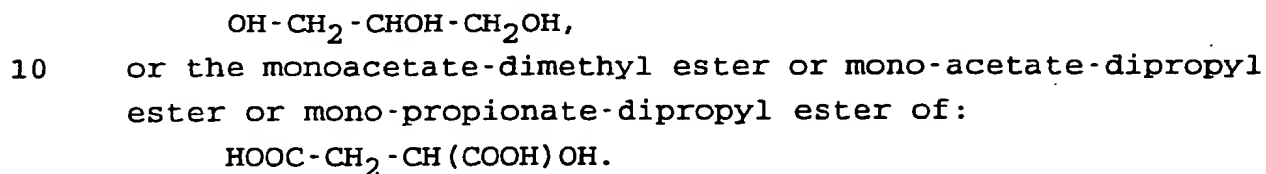
31. A composition according to claim 31, wherein the compound has the formula:



32. A composition according to claim 31, wherein the compound has the formula:



33. A composition according to claim 26, in which the compound is the diacetate or dipropionate of:



15 34. A composition according to any preceding claim, wherein the concentration of the compound in the composition is from about 3% to about 60% by weight based on the weight of the composition and preferably wherein the concentration of the compound in the composition is from about 8% to about 18% by weight based on the weight of the composition.
20

35. A composition according to any preceding claim, which further comprises, in an amount of up to 40% by weight of the total composition, one or more compounds selected from
25 the group of water-soluble and/or water-swellaable polymers, which water-soluble and/or water-swellaable polymer preferably are selected from group consisting of alkenol homopolymers and alkenol copolymers.

30 36. A composition according to the preceding claim, wherein said water-soluble and/or water-swellaable polymer is selected from group consisting of alkenol copolymers which contain vinyl alcohol units as well as aliphatic units such as are obtained by copolymerization of vinyl
35 acetate with a member selected from ethylene, propylene, isobutylene and/or styrene with subsequent hydrolysis of the vinyl ester group, whereby the hydroxyl group content is such that the copolymerized polymer is at least water-swellaable.

37. A composition according to any preceding claim, further comprising, in an amount up to 60 % by weight of the total composition, one or more hydrophobic thermoplastic polymer(s) which is/are substantially water-insoluble.

38. A composition according to claim 37, wherein said polymer contains a member selected from the group consisting of: hydroxyl-, ether-, acid-, ester- and urethane groups, and mixtures thereof.

39. A composition according to claim 37, wherein said polymer is selected from the group consisting of ethylene/vinyl acetate-copolymers, ethylene/vinyl alcohol-copolymers, ethylene/acrylic acid-copolymers, ethylene/ethyl acrylate-copolymers, ethylene/methacrylate-copolymers, polyurethane-copolymers, styrene/acrylonitrile-copolymers; polyacetals and mixtures thereof.

40. A composition according to claim 39, wherein said polymer is selected from the group consisting of ethylene/vinyl alcohol-copolymers with an ethylene content of about 10 mol% to about 50 mol%, preferably an ethylene content of about 15 mol% to about 48 mol%, and most preferably an ethylene content of about 40 mol% to about 48 mol%.

41. A composition according to any preceding claim, further comprising at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, stabilisers, colouring agents, flame retardants, boron-containing compounds and alkali and alkaline earth metal salts, and cellulose fibres.

42. A composition according to the preceding claim, wherein the filler is selected from the group consisting of wood derived materials, and oxides of magnesium, aluminum, silicon, and titanium.

43. A composition according to the claim 41, in which the other plasticisers are selected from the group consisting of low molecular weight poly(alkylene oxides); poly(ethylene-propylene glycols); pentaerythritol; 5 propylene glycol; sorbitol; sodium diethylsulfosuccinate; and phosphatides.

44. A composition according to claim 41, in which the flame retardants are selected from the group consisting of 10 diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorous oxide; aliphatic phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2- 15 ethylhexyl diphenyl phosphate; tributoxyethyl phosphate; guanidinium phosphate; bis(hydroxypropyl) sec.butyl phosphine oxide; polypropoxylated dibutyl pyrophosphoric acid; a mixture of phosphonic acid, methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl methyl ester, P- 20 oxide and phosphonic acid, methyl-, bis [(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl] ester, P,P'-dioxide; ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous, guanidinium sulfate; 25 ammonium sulfate; ammonium sulfamate; and tetrakis (hydroxymethyl) phosphonium sulfate, ammonium polyphosphate and/or ethylenediamine polyphosphate, guanidinium phosphate, ammonium sulphate and/or guanidinium sulfate.

30

45. A composition according to any preceding claim, when in the form of a melt.

46. A composition according to claim 45, when in the form 35 of a solid shaped articles, including a granulate or pellet.

47. The composition of claim 45, when shaped into articles by a process selected from the group consisting of:

injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, co-extrusion, foaming, and combinations thereof.

- 5 48. A finished article made from the melt according to claim 45, the article being selected from the group consisting of bottles, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, foams, granules and powders.

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49. The use of a compound having a molecular weight of less than about 3,000 and having at least one ester group and optionally further comprising at least one hydroxyl group as a processing aid in the manufacture of a composition comprising at least one derivative of a starch, and optionally one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

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50. A method of preparation of a composition according to any one of claims 1 - 45, comprising: (i) drying or conditioning a composition comprising a derivative of a starch to a moisture content of less than about 5%, (ii) admixing to said composition before, during or after drying, at least one compound having a molecular weight of less than about 3,000 and having at least one ester group and optionally further comprising at least one hydroxyl group and (iii) melting and plasticising the mixture until a uniform melt is obtained.

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51. A method of preparation of a composition according to any one of claims 1 - 45, comprising: (i) melting and plasticising a composition comprising a derivative of starch, and at least one compound having a molecular weight of less than about 3,000 and having at least one ester group and optionally further comprising at least one hydroxyl group, until a uniform melt is obtained and (ii) drying the mixture during or after melt formation and/or plastification to a moisture content of less than 5%, by

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weight of the total composition.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/02895

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08L3/04; C08K5/10; C08K5/11		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08K ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 394 803 (BATTELLE-INSTITUT) 31 October 1990 see example 1 ---	1-51
Y	EP,A,0 459 560 (CARGILL B.V.) 4 December 1991 see page 2, line 26 - line 33 ---	1-51
A	US,A,3 074 803 (JOHN F. MCGOWAN) 22 January 1963 ---	
P,X	WO,A,9 219 675 (BATTELLE-INSTITUT) 12 November 1992 see examples 5,6,7 -----	1-51
<p>¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 19 JULY 1993	Date of Mailing of this International Search Report 19 JUL 93	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer LENSEN H.W.M.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302895
SA 72428

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19/07/93

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		CA-A- 2025424	16-03-91
US-A-3074803		None	
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		AU-A- 1656792	21-12-92
		CA-A- 2086410	31-10-92
		EP-A- 0537317	21-04-93

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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